CHANGE OF ELECTRICAL CONDUCTIVITY OF CdS SINGLE CRYSTALS DURING HEAT TREATMENTS IN SULFUR VAPOR BETWEEN 500° and 700°C

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CHANGE OF ELECTRICAL CONDUCTIVITY OF CdS SINGLE CRYSTALS DURING HEAT TREATMENTS IN SULFUR VAPOR BETWEEN 500° AND 700°C *

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ABSTRACT

The electrical conductivity of CdS single crystals was measured, using a four-electrode method, as a function of the S vapor pressure in the range from 10 to 1000 Torr in a double furnace allowing for independent variation of the crystal temperature and S-vapor pressure. In agreement with earlier measurements, the current was observed to decrease with increasing S-vapor pressure following a power law $\sigma \propto p^{-1/m}$. The exponent 1/m depends on the crystal temperature and is about 1/24 for $500^\circ < T < 520^\circ$, 1/4 for $530^\circ < T < 630^\circ$, and about 1/12 for $640^\circ < T < 700^\circ$C. A simple model using S vacancies, Cd interstitials and Cd vacancies is used to explain the observed behavior. Doubly ionized S vacancies are assumed to be predominant in the lowest temperature range, single ionized Frenkel defects in the intermediate temperature range, and doubly ionized

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Cd interstitials in the highest temperature range.

Although the electrical and optical properties of cadmium sulfide single crystals are known to be influenced by intrinsic defects, the precise nature and identity of these defects is still subject to much speculation. Some conclusions concerning the defect structure can be formulated from measurements of the steady state conductivity during heat treatments in a sulfur atmosphere at temperatures above 500°C.

The theory of equilibrium between the crystal and sulfur vapor at high temperatures predicts a power law dependence of the concentration of intrinsic defects on the sulfur vapor pressure. The power law exponent is related to the average number of atoms in the sulfur molecule and to the degree of ionization of the defect.

In the present investigation approximately 10 undoped cadmium sulfide platelets of high crystallographic quality were used. The crystals were grown in an inert atmosphere with 4% H_2S at about 1100°C by sublimation of spectral grade microcrystals. The surfaces were free of striations. At

temperatures above 500°C all crystals behaved similarly; the only noticeable difference was that the thicker crystals required more time to equilibrate.

The first figure depicts the environmental system which was used to control the temperature and pressure of the crystal and sulfur independently. Basically the system consists of two quartz chambers joined concentrically by a smaller tube. Only gold and quartz were used in the portions of the system that came in contact with the sulfur vapor because they would not react with the sulfur vapor under the experimental conditions.

The crystal was mounted on a detachable crystal holder. The crystal and four gold electrodes were held in place on a quartz base with four quartz springs.

The other half of the system contained sulfur.

Movable Pt/Pt;Rh thermocouples enclosed in quartz envelopes were used to measure the temperature in both halves of the system.

The temperatures of the two halves were regulated independently to within 1/2°C with a double oven. By requiring that the crystal temperature always be greater than the sulfur temperature and that liquid sulfur always be present in equilibrium with the sulfur vapor, the sulfur pressure is determined by the temperature of the molten sulfur.

After outgasing the sulfur and evacuating the system to a pressure of 10^{-6} Torr, the dependence of the stationary dark current on the sulfur pressure was investigated. The sulfur pressure ranged from 0.1 to 800 Torr. Crystal temperatures ranged from 500°C to 700°C.

The conductivity measurements were performed using the standard four point probe technique with 6 volts applied to the crystal.

The problem of establishing and maintaining electrical contact with the crystal was the greatest source of difficulty in this experiment. Evaporated contacts of gold, platinum, and other materials which supposedly would not react with the sulfur vapor were tried without success. They either diffused into the crystal or reacted with the atmosphere. The best long-term results were obtained with heavy gold wires pressed onto the crystal by quartz springs. The contacts were "formed" by intermittently applying 300 volts to the crystal at a temperature of 500°C. The peak currents were about 1 ma. in this case.

Figure 2 is a plot of the stationary dark current for one of the crystals as a function of the sulfur pressure for different crystal temperatures. In regions of low sulfur pressures at the lower crystal temperatures the current is practically independent of sulfur pressure.

This is probably attributable to uncompensated donors and is not of much interest at this time. For higher pressures the power law relationship holds. In this region the current is proportional to the sulfur pressure raised to the power minus 1/m.

The dependence of m on crystal temperature is indicated in the next figure.

In figure 3, m is plotted as a function of crystal temperature. Clearly, there are three regions which are defined by a dramatic shift in the value of m.

We can express m as an integral multiple of the average number of atoms in the sulfur molecule. Strictly speaking, the average number of atoms in the sulfur molecule is not well known in this experiment because of the differential temperature in the two halves of the system. It is safe to assume, however, that it lies between 8 and 5 atoms, decreasing with increasing crystal temperature in the temperature range under consideration.

If x represents the average number of atoms in the sulfur molecule, then the three regions are characterized by m's of 3x, x, and 3x respectively.

In figure 4, using Krőeger's formulation of the theory of intrinsic defects,we can interpret the results in terms of a point defect model which consists of doubly ionized

sulfur vacancies, and singly and doubly ionized cadmium interstitials. In each region we assume that there is one defect which is dominant.

Region I can be characterized by doubly ionized sulfur vacancies in equilibrium with the sulfur vapor. The equilibrium reaction may be formulated by the first equation. By applying the law of mass action and assuming the electron density to be twice the density of sulfur vacancies. we obtain the observed dependence of current on sulfur pressure.

The second region is explained by assuming a transition to Frenkel disorder in the cadmium sublattice involving singly ionized defects. A possible equilibrium reaction is given by the first equation of the second group. Application of the law of mass action and the Frenkel condition gives the observed dependence in this region.

In region III the dominant defect is the doubly ionized cadmium interstitial. Using the condition that the electron density is twice the density of doubly ionized cadmium interstitials, we obtain the experimental dependence.

This proposed model is perhaps the most economical model which agrees with the other experimental evidence. The model is somewhat naive in that defect associates have not been considered here. Further experiments in this area are necessary for more definite conclusions.

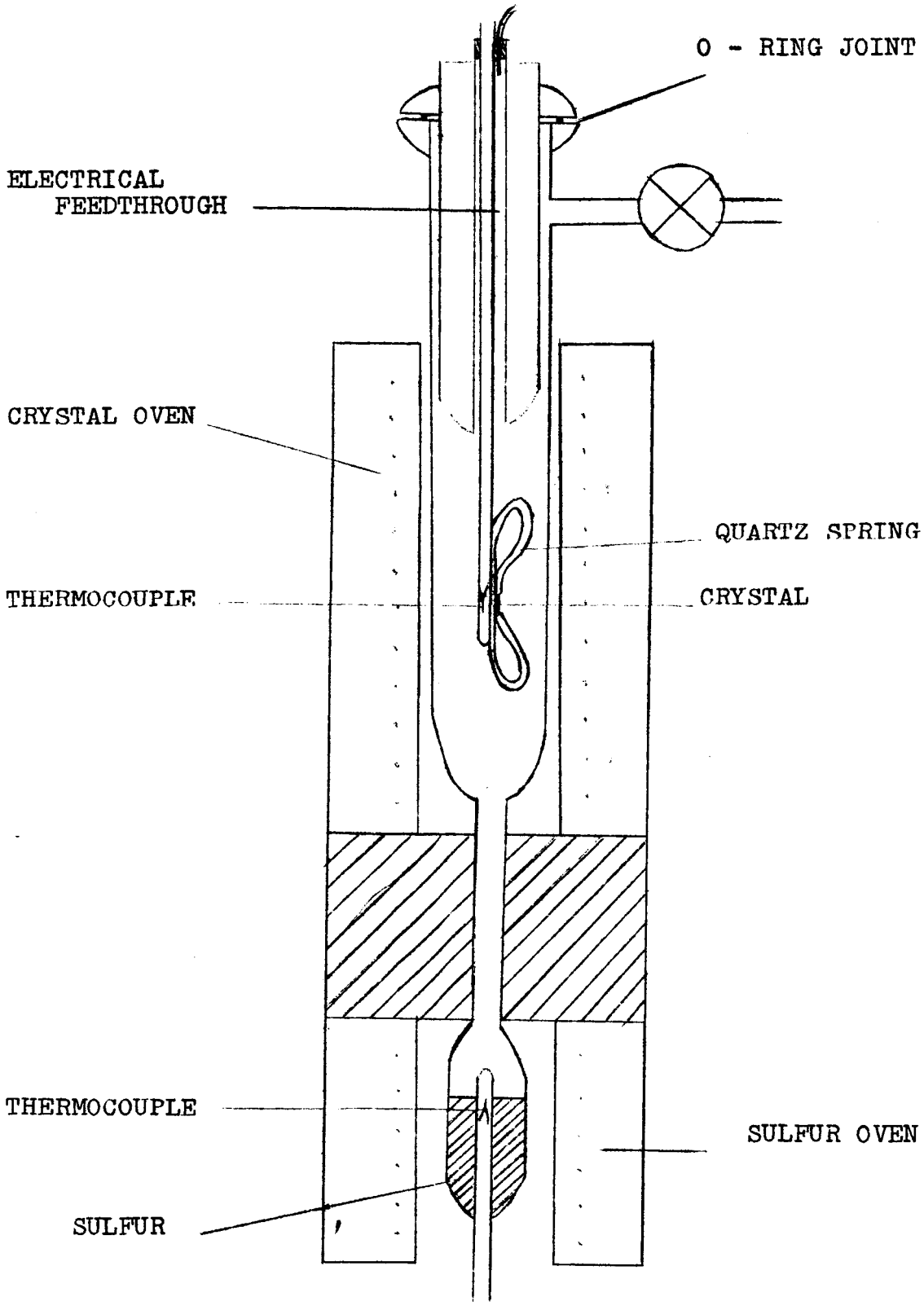
O - RING JOINT
ELECTRICAL FEEDTHROUGH
CRYSTAL OVEN
QUARTZ SPRING
THERMOCOUPLE
CRYSTAL
THERMOCOUPLE
SULFUR OVEN
SULFUR

Figure 1

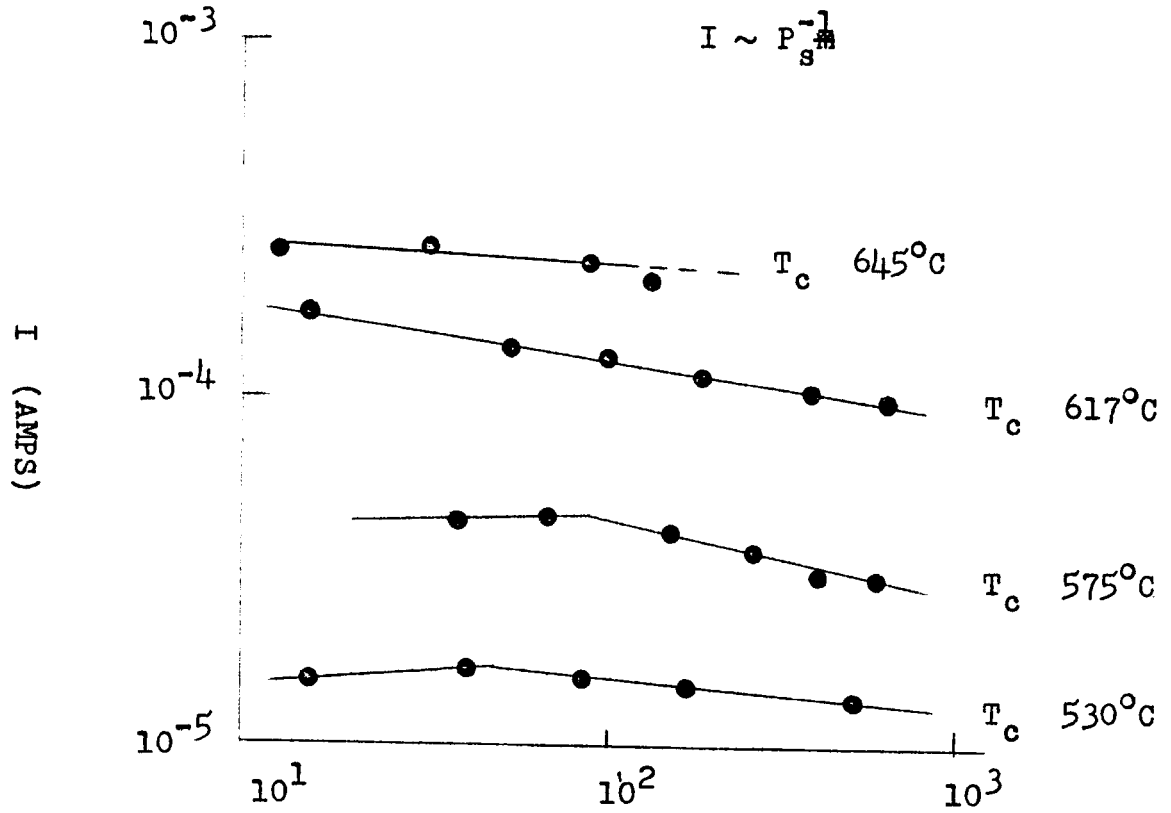
10^{-3}
$I \sim P_s^{-\frac{1}{m}}$
T_c 645°C
10^{-4}
T_c 617°C
T_c 575°C
T_c 530°C
10^{-5}
I (AMPS)
10^1
10^2
10^3
SULFUR PRESSURE (TORR)

Figure 2

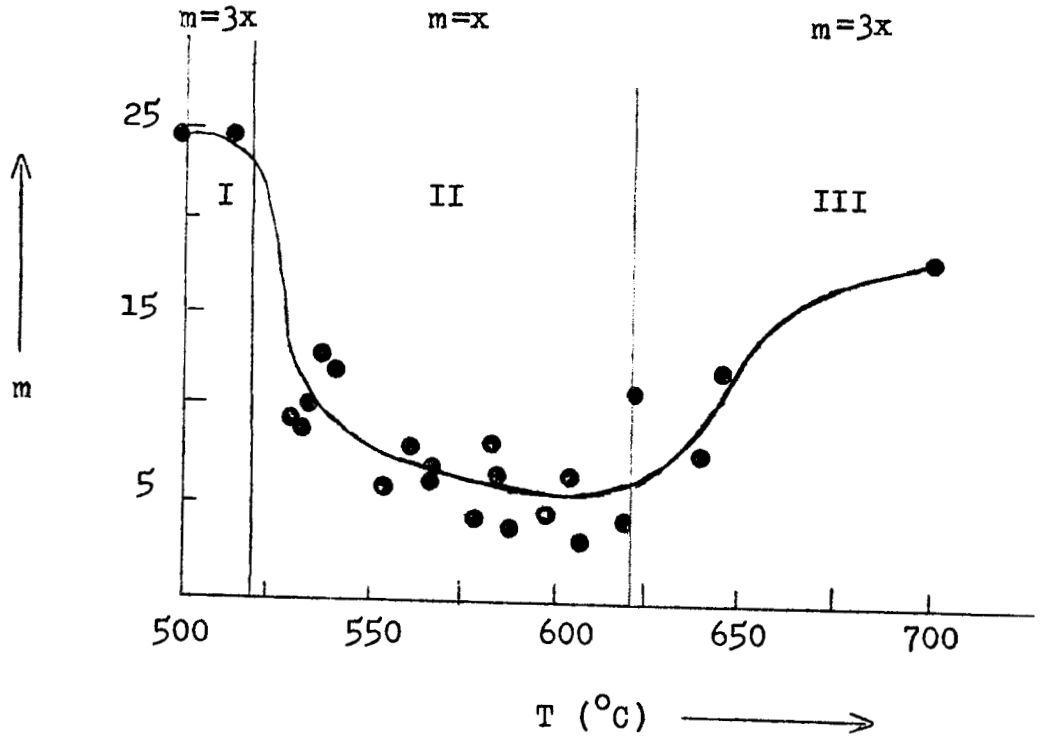

Figure 3

DEFECT MODEL

Region I DOUBLY IONIZED SULFUR VACANCIES $T < 520^{\circ}C$

$$\frac{1}{x} S_x + 2\theta + V_s^{\bullet\bullet} \rightleftarrows S_s$$

$$n^2[V_s^{\bullet\bullet}] \sim p_s^{-1/x}$$

$$n \sim 2[V_s^{\bullet\bullet}]$$

$$i \sim n \sim p_s^{-1/3x}$$

Region II SINGLY IONIZED FRENKEL DEFECTS $520^{\circ}C < T < 620^{\circ}C$

$$\frac{1}{x} S_x + \theta + Cd_i^{\bullet} \rightleftarrows CdS$$

$$n[Cd_i^{\bullet}] \sim p_s^{-1/x}$$

$$[Cd_i^{\bullet}] \sim [V'_{Cd}] \text{ const.}$$

$$i \sim n \sim p_s^{-1/x}$$

Region III DOUBLY IONIZED CADMIUM INTERSTITIALS $620^{\circ}C < T$

$$\frac{1}{x} S_x + 2\theta + Cd_i^{\bullet\bullet} \rightleftarrows CdS$$

$$n^2[Cd_i^{\bullet\bullet}] \sim p_s^{-1/x}$$

$$n \sim 2[Cd_i^{\bullet\bullet}]$$

$$i \sim n \sim p_s^{-1/3x}$$

Figure 4